AD-A198 981

REPORT DOCUMENTATION PAGE

1b RESTRICTIVE MARKINGS	
2b DECLASSIFICATION / DOWNGRADING SCHEDULE	3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for Public Distribution - Unlimited
4 PERFORMING ORGANIZATION REPORT NUMBER(S) 1	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION Columbia University/Dept. of Chemical Engr. & Appld Chem.	6b OFFICE SYMBOL (If applicable)
7a NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c ADDRESS (City, State, and ZIP Code) 500 W. 120 St./ 351 Engineering Terrace New York, NY 10027	7b ADDRESS (City, State, and ZIP Code)
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b OFFICE SYMBOL (If applicable)
9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
Proton Mobility in Liquid and Frozen $HClO_4 5.5H_2O$ - NMR and Conductivity Measurements

12 PERSONAL AUTHOR(S)
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13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical	FROM 8/11/88 TO 7/15/89	7/1/88	12

16 SUPPLEMENTARY NOTATION

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

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20 DISTRIBUTION / AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	
22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K0642

R&T Code 4133014

Technical Report No. 1

PROTON MOBILITY IN LIQUID AND FROZEN $HC10_4 5.5H_20$ - NMR AND CONDUCTIVITY MEASUREMENTS

by

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July 1988

Accepted for publication in J. Phys. Chem.

PROTON MOBILITY IN LIQUID AND FROZEN $HClO_4 \cdot 5.5H_2O$ - NMR AND CONDUCTIVITY MEASUREMENTS

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Abstract

^2H NMR spectra and conductivity of liquid and frozen $HClO_4$ 5.5 H_2O have been obtained over wide temperature range (140 to 300K). The ^2H NMR spectra show a gradual broadening of an isotropic resonance at lower temperature from $\Delta\nu_{1/2}$ = 2Hz at 300K to 50 kH_z at 170K. At even lower temperatures, flat top spectra of breadth 170 kH_z were observed. The presence of isotropic spectra above 170°K indicates that the deuterons (protons) are relatively mobile even in the frozen state. A plot of ln $(1/\Delta\nu_{1/2})$ vs. (1/T), the Arrhenius plot, further reveals the presence of two phase transitions centered at 228 ± 2K and 180 ± 5K. Conductivity measurements agree well with the NMR results. The activation energies were determined from NMR (conductivity) measurements to be 0.27 eV (0.29 eV) from 228-180K and 0.40 eV (0.36 eV) from 180 to 140K.

Introduction

In recent studies it has been shown that the investigation of processes at the metal - aqueous electrolyte interface can be extended to temperatures below the freezing point of the electrolyte, and it has been demonstrated for reactions as well as double layer properties [1-3]. The electrolyte that has been used in these investigations was aqueous perchloric acid of the composition $HClO_4$*5.5H_2O. In the phase diagram of H_2O-$HClO_4$ this composition represents an acidhydrate of a stoichiometric composition with the highest water content possible. The freezing point of that compound is 228K. Recently the structure of $HClO_4$*5.5H_2O was determined by Mootz et al. [4,5] using X-ray diffraction. According to Mootz and Wiebke [4] the compound crystallizes in a clathrate structure, similar to several gas hydrates, of the cubic 12Å type. H_2O and H^+ form the host lattice while ClO_4^- is the guest. At temperatures T < 173K a higher order phase transformation seems to

take place which is reversible upon going back to higher temperatures.

Since this perchloric acid hydrate is a suitable electrolyte also in the frozen state it was assumed that the protons are relatively mobile even in the solid phase. In order to clarify this point, NMR and conductivity measurements were performed to obtain some insight into the proton mobility of $HClO_4$*$5.5H_2O$ at various temperatures in the liquid and frozen state of the electrolyte.

Experimental

The conductivity measurements were performed using an a.c. bridge technique (1kHz) and fast galvanostatic pulses. The latter technique does only give the resistance and a calibration was used to obtain conductivity values. The cell consisted of two platinum foils, each of approx. 2 cm^2 area, which were positioned approx. 1mm apart from each other. The cell is similar to the one described earlier [3] and had a temperature accuracy of approx. ± 2K. Measurements were performed in an aqueous solution of $HClO_4$ (ACS grade) which corresponds to the composition of the 5.5 hydrate. Measurements were not performed in deuterated solutions. The difference between H^+ and D^+ was not considered crucial for this preliminary study. The conductivity was measured as a function of temperature from higher to lower temperatures and vice versa.

Deuterium NMR quadrupolar spectra were obtained on a home-built 300 MH_z spectrometer (^2H frequency - 46 MHz) interfaced to a Nicolet 1280 computer data system with 293B pulse programmer and a 2090 transient recorder capable of digitizing up to 2 Mhz at 12 bit resolution. Spectra without proton decoupling were obtained using either a single pulse sequence for temperatures

above 190 K where T_2, the spin-spin relaxation time, is long, a quadrupolar echo technique /6/ for temperatures below 190 K ($P_{\pi/2}$ = 2 microsecond). Recycle delay times were varied between 0.2 to 4 s depending on temperature. Samples were cooled with temperature regulated nitrogen gas at 50 cubic feet per hour. Between 10-15 minutes were allowed for sample to equilibrate between temperature changes. The complete equilibration normally takes 3 minutes as monitored by NMR. Temperatures were calibrated with a platinum resistor placed inside a calibration sample and the accuracy is estimated to be $\pm$ 2°C. The sample for the NMR measurements was a 5mm x 1.5 cm sample tube contains 0.25 ml of $HClO_4$ $5.5H_2O$ which was prepared by mixing 3.22g D_2O with 7.08g of 71% $HClO_4$, this corresponding to D:H molar ratio of approximately 1.1.

Results and Discussion

The results of the conductivity measurements are shown in Fig. 1 in an Arrhenius plot. Essentially three different ranges can be distinguished. In the liquid electrolyte, above 228K, the activation energy of the conductivity is small, approx. 0.02eV. After freezing of the electrolyte, no discontinuity seems to appear in the conductivity but the activation energy becomes much larger, 0.29eV. This value is still relatively small for an ionic conduction process. At lower temperatures, T<180K, a further change of slope is observed. The activation energy calculated from the slope is approx. 0.37eV, slightly higher than the one at higher temperatures.

Fig. 2 shows deuterium quadrupole spectra of the aqueous perchloric acid at various temperatures. The temperature dependence of the NMR spectra shows two prominent features: (i) a gradual broadening of the high temperature isotropic line from 2Hz at 293K to 28 kHz at 171K and (ii) a sharp transition

from an isotropic line to a broad spectrum at 170 ± 4K. Also shown in Fig. 2 is a deuterium quadrupole spectrum of pure D_2O at 243K. The D_2O spectrum has breadth, the separation of the two prominent edges, of ~ 170 kHz and asymmetry parameter η ~ 0.1. This is characteristic of immobilized deuterons. The breadth of the deuterium quadrupole spectrum of perchloric acid deuterons at 153K is also ~ 170kH$_z$. However, the presence of flat-top lineshape indicates that the deuterons in $HClO_4$*5.5H_2O are still reorienting at ~ 10^4 s^{-1} /9-11/.

Fig. 3 shows the temperature dependence of ℓn ($1/\Delta\nu_{1/2}$), where $\Delta\nu_{1/2}$ is the half width of the isotropic resonance above 170K. This plot reveals additional information on the nature of the electrolyte system. Two transitions with the midpoint of the transition, T_m, at 228 ± 2K and 18[illegible] ± 5K are observed. A complex supercooling effect was observed for the high temperature transition. When the temperature was decreased from above T_m, the complete transformation did not occur until ~ 208K. This transformation is characterized by the observation of a single narrow isotropic deuterium spectrum whose linewidth increases with decreasing temperature. However, when the temperature was raised from 208 to 228K, the deuterium spectrum consists of two components, a broad component characteristic of the low temperature phase and a narrow component characteristic of the highly mobile phase. The relative population of these two components varies with temperature in the sense that high temperature favors the mobile component. The nature of this complex behavior is currently under investigation. The low temperature T_m agrees quite well with our conductivity measurements. The observation of isotropic lines at the temperatures where perchloric acid is frozen, i.e., below 228K, provides direct evidence that deuterons are quite mobile in this solid perchloric acid clathrate.

Line narrowing can take place through three mechanisms, the diffusion of deuterons from site to site in the clathrate lattice [12], the 180° reorientation of the water molecule with respect to the H-O-H bisector without diffusion, and the coexistence of reorientation and diffusion. In the fast limit, the diffusion process averages the deuterium spectrum to an isotropic line whereas a broad, $\eta=1$ spectrum of breadth ~ 120 kH_z is expected for the anisotropic reorientation process alone [7,9]. Our observation of isotropic lines above 170K suggests that reorientation of deuteron alone can not explain the observation and that the deuteron must be diffusing rapidly through the lattice. The correlation time of the diffusion process is related to the increase in linewidth, $\Delta\nu_{1/2}$, by the following equation [13,14].

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2} = \frac{12\pi}{8}\left(1 + \eta^2/3\right)\left\{\frac{e^2qQ}{h}\right\}^2 \tau_c \qquad (1)$$

where T_2 is the spin-spin relaxation time, η is the asymmetry parameter, e^2qQ/h is the quadrupole coupling constant (~ 200 kHz) and τ_c is the correlation time for the diffusion process. Since η ~ 0.1 for deuterons in water, the asymmetry contribution is negligible and the linebroadening can be related to the correlation time τ_c and hence the diffusion rate $k = 1/\tau_c$, as

$$k = C \cdot \Delta\nu_{1/2} \qquad (2)$$

where $$C = \frac{12\pi}{8}\left\{\frac{e^2qQ}{h}\right\}^2$$

Therefore a plot of $\ln(1/\Delta\nu_{1/2})$ vs. $1/T$ will allow us to determine the

activation energy for the reorientation process. This is shown in Fig. 3. The activation energies were found to be 0.04 ± 0.02 eV (above 230 K), 0.27 ± 0.05 eV (180-228K) and 0.4 ± 0.1 eV (170-180 K). These agree quite well with that obtained from conductivity measurements of 0.02 eV, 0.29 eV and 0.36 eV, respectively. Since conductivity measurements monitor the diffusion process it is tempting to conclude that the narrowing of the deuterium spectrum is also due to diffusion. However, it is not necessarily so. Soda and Chiba has measured the activation energies of the reorientation process of several hydrates and found them to vary between 0.25 to 0.7 eV 9/. Garg and Davidson have employed the second moments of the proton NMR spectra to determine the dynamics of Class I and II clathrate ices and have concluded that although reorientation may produce line narrowing at somewhat lower temperatures than diffusion, the two processes appear to be effective in nearly the same temperature range 10 . Therefore the NMR spectral averaging is likely to be the combined effect of reorientation and diffusion. We should also point out that at lower temperatures (below 180K) the extreme narrowing condition, i.e., $w\tau_c \ll 1$, may not be valid, therefore the activation energy obtained at these low temperatures must be taken with caution.

Recently using deuterium NMR spin-alignment technique, Fujara et al., have measured the geometry and time scale of the tetrahedral jump of ^2H in deuterated polycrystalline hexagonal ice (Ih) 12 . They also concluded that these tetrahedral jumps are due to diffusing Bjerrum vacancies. If one assume that diffusion is responsible for the NMR spectral averaging, then one can determine the diffusion rate of deuteron from the following equation

$$D = \frac{\bar{x}^2}{2\tau_c} \qquad (3)$$

where $\bar{x} = 3\text{Å}$ is the separation of deuteron in the clathrate lattice and τ_c is the correlation time of the diffusion process which can be taken as the time it takes for the deuteron to hop from site to site. The calculated diffusion constants follow the same curve as $\pi \cdot 1/\Delta\nu_{1/2}$ and are shown in Fig. 3. They vary from $\sim 10^{-6}$ cm^2/s at 260 K to $\sim 3 \times 10^{-10}$ cm^2/s at 170 K. Freezing of the electrolyte at 228 K reduces the diffusion constant by a factor of 7 from $\sim 4 \times 10^{-7}$ to $\sim 5.8 \times 10^{-8}$ cm^2/s.

When we compare our results with data obtained from X-ray diffraction [4,5] there is a quite good agreement. The clathrate structure which was determined for $HClO_4 * 5.5H_2O$ contains large voids and in assigning the diffraction patterns the authors reported that no sharp reflexes could be obtained for the protons. This already indicates that the protons exhibit a large mobility in the solid matrix. The higher order phase transformation found at 173K coincides well with the changes in slope found in the Arrhenius plots of the conductivity and also the NMR data. The rearrangement of the lattice at this temperature makes the motion of the protons obviously less favorable. In conclusion, our conductivity and NMR data shows that the deuteron (proton) in the $HClO_4 * 5.5H_2O$ clathrate are very mobile even in the frozen state and that two structural transitions are observed which are centered at 228 ± 2 K and 180 ± 5 K.

Acknowledgements

This work has been supported in part by the National Science Foundation PCM-8313208 (T.-H.H.), PCM-8309335 (T.-H.H.) and CHE8605698 (U.S.) and the Office of Naval Research (U.S.).

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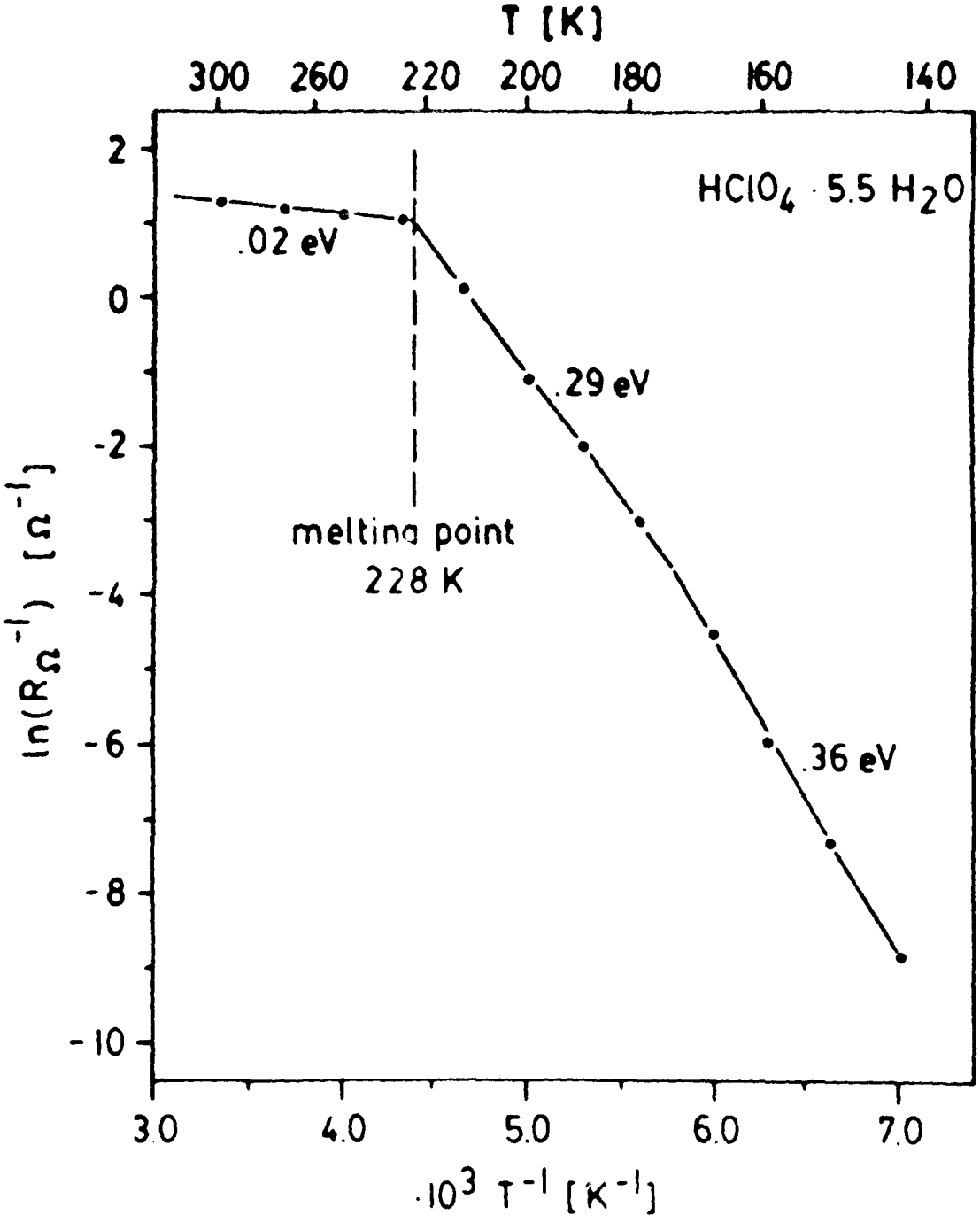
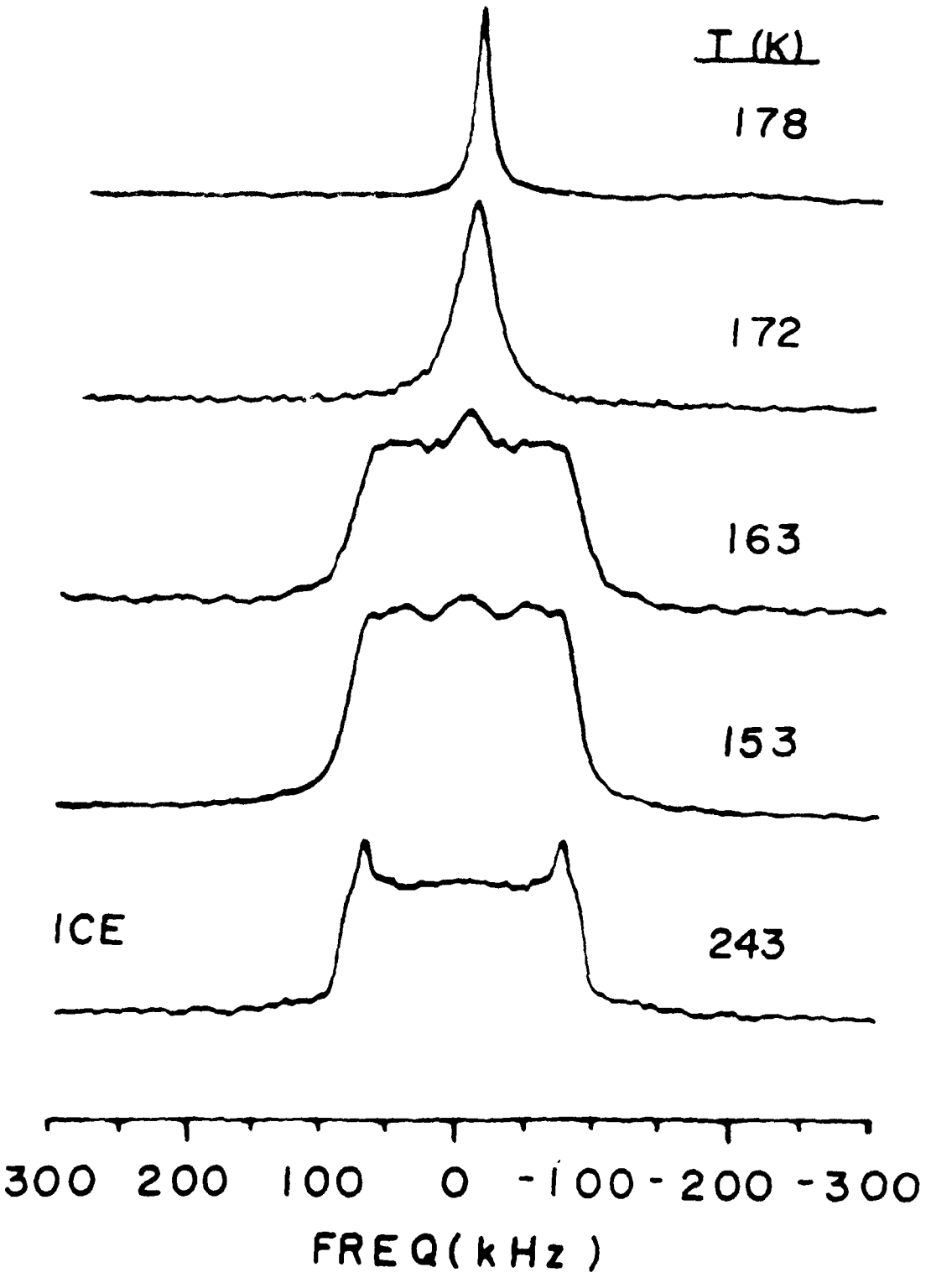
Figure Captions

Fig. 1. Arrhenius plot of the electrical conductivity of $HClO_4*5.5H_2O$ in the temperature range 140 - 300K.

Fig. 2. Deuterium quadrupole NMR spectra of the perchloric acid hydrate at various temperatures. Spectra were obtained with the quadrupole echo technique with $\tau_{90°}$ = 2 μs and digitized at 1 MHz. Recycle times were varied from 0.2S (173K) to 4S (153K). Also shown on the figure is a spectrum of D_2O at 243K (bottom). See text for details.

Fig. 3. The temperature variations of deuterium quadrupole NMR spectral linewidth, $W_{1/2}$ (Hz) and diffusion constant, D (cm^2/s). The linewidths were determined by lineshape simulation on a Nicolet 1280 computer using NMRCAP program.


T [K]
300
260
220
200
180
160
140
2
0
-2
-4
-6
-8
-10
$HClO_4 \cdot 5.5\ H_2O$
.02 eV
.29 eV
.36 eV
melting point
228 K
$\ln(R\Omega^{-1})$ $[\Omega^{-1}]$
3.0
4.0
5.0
6.0
7.0
$\cdot 10^3\ T^{-1}\ [K^{-1}]$


T (K)
178
172
163
153
ICE
243
300 200 100 0 -100 -200 -300
FREQ(kHz)

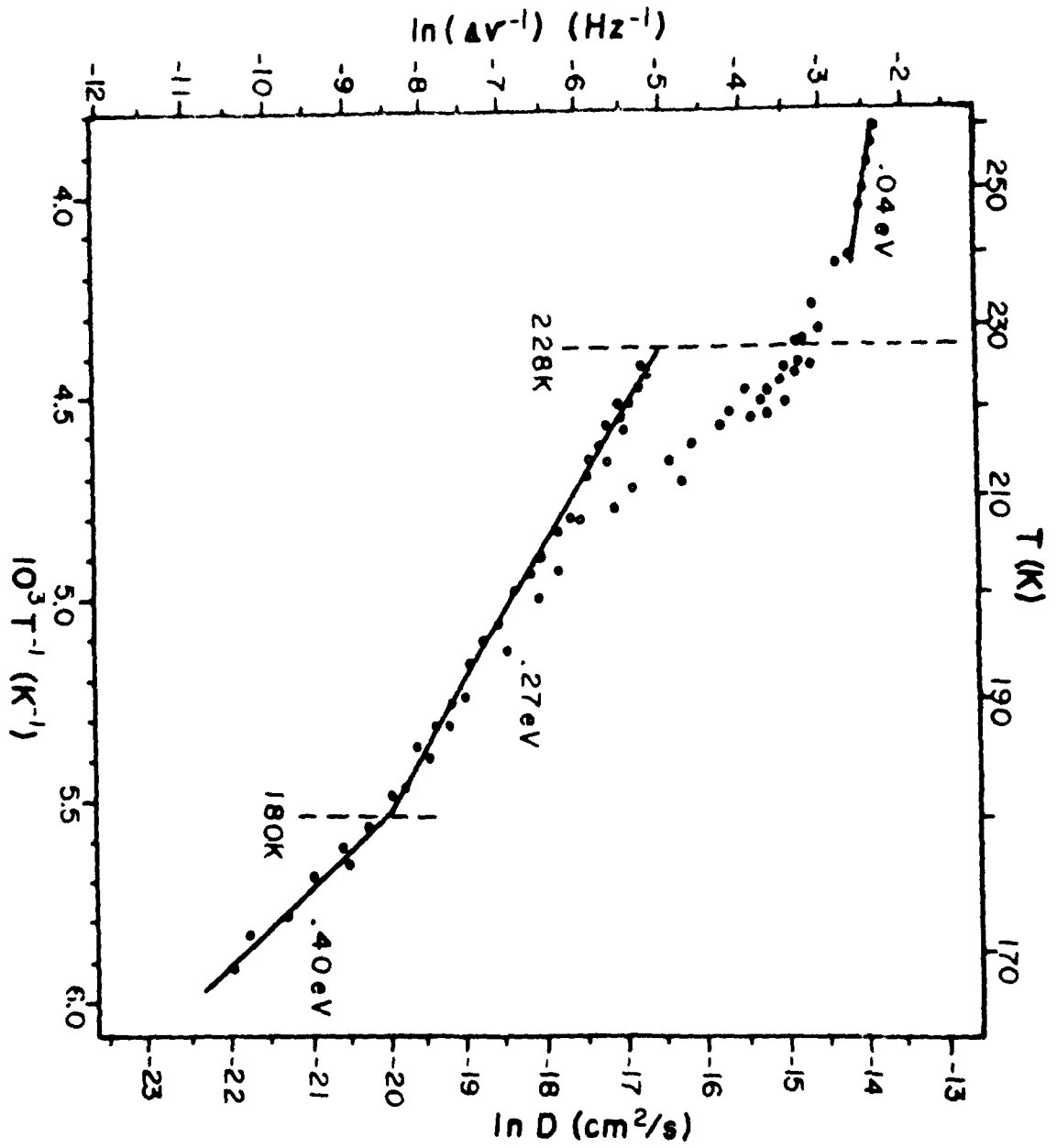

ln(Δν⁻¹) (Hz⁻¹)
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
4.0
4.5
5.0
5.5
6.0
10³T⁻¹ (K⁻¹)
250
230
210
190
170
T (K)
.04eV
228K
.27eV
180K
.40eV
-23
-22
-21
-20
-19
-18
-17
-16
-15
-14
-13
ln D (cm²/s)

Fig. 3